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# Progress in the Determination of $^{227}\text{Ac}$ in Sea Water

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## **Abstract**

$^{227}\text{Ac}$  is a naturally occurring radioisotope with a unique combination of properties that make it suitable for the determination of deep ocean mixing and upwelling rates. Here, we present a method for the determination of  $^{227}\text{Ac}$  in sea water on sample sizes of 20-80 l. The measurement is based on co-precipitation of  $^{227}\text{Ac}$  with  $\text{MnO}_2$ , followed by chemical isolation of actinium in presence of an artificial Ac isotope. Actinium is then electrodeposited onto silver discs. In two alpha-spectrometric counting periods, first the artificial  $^{225}\text{Ac}$  isotope is counted, then after >100 days five daughters of  $^{227}\text{Ac}$ . The first counting period gives a total yield for the procedure, integrating chemical recovery and detector efficiency. The total yield was found here to be on average  $15 \pm 5 \%$ , the chemical yield on average about 50%. The counting of five decay products of  $^{227}\text{Ac}$  in the second period makes the method particularly sensitive. Using appropriate decay corrections, the initial  $^{227}\text{Ac}$  activity can be determined to better than 10% relative error for concentrations <10000 atoms/L. We compare data acquired

by the new method to a data set from in-situ pumps, from a parallel sampling campaign in the Eastern Weddell Gyre, and we can show excellent agreement. Repeated determinations of  $^{227}\text{Ac}$  in a uranium reference material (UREM-11) demonstrate the accuracy of the method.

Keywords: actinium, upwelling, vertical mixing, diapycnal mixing, alpha spectrometry, ocean

## 1. Introduction

The distribution of the naturally occurring radioisotope  $^{227}\text{Ac}$  in the ocean is of particular interest for studies on deep water mixing and upwelling (Nozaki, 1984). A fraction of the total  $^{227}\text{Ac}$  activity found in the ocean is supported by the presence of  $^{231}\text{Pa}$  in sea water, which continuously produces  $^{227}\text{Ac}$  until a secular equilibrium is reached. Another variable fraction of  $^{227}\text{Ac}$ , called  $^{227}\text{Ac}_{\text{excess}}$  or  $^{227}\text{Ac}_{\text{ex}}$ , is exceeding this supported value. It originates from  $^{231}\text{Pa}$  in sediments, and it is distributed in the ocean by mixing (Nozaki, 1993). The source term of  $^{227}\text{Ac}_{\text{ex}}$  is dominated by release from the deep-sea floor (Nozaki and Yang, 1987; Nozaki et al., 1990; Geibert et al., submitted;). Once in the water column, the activity of  $^{227}\text{Ac}_{\text{ex}}$  is controlled by radioactive decay with a half-life of 21.77 years, and mixing. This combination of properties makes it ideally suited for the calculation of deep-sea diapycnal mixing coefficients (Nozaki, 1993), and, under certain circumstances, the estimation of upwelling rates (Geibert et al., 2002).

This exclusive information is available naturally, which offers advantages compared to studies with artificial tracers like  $\text{SF}_6$  (e.g. Ledwell et al., 2000), because no addition of tracers to the ocean is required. However,  $^{227}\text{Ac}$  has never been measured routinely, which has to do with the fact that no simple measurement technique was available so far. Several hundred litres of sea water had to be processed for each measurement. The applied methods were either based on counting of the  $^{227}\text{Ac}$  daughter  $^{227}\text{Th}$  (Nozaki and co-workers; Geibert and co-workers), or on counting of the grand-daughter isotope  $^{219}\text{Rn}$  by the delayed coincidence counting system, as described by Moore and Arnold (1996), Shaw and Moore (2002), or Geibert et al. (submitted). The actual use of  $^{227}\text{Ac}$  as a tracer in marine science

depends on a possibility to reliably measure it on samples that can be taken by bottles, like e.g. a Niskin system.

The concentrations of  $^{227}\text{Ac}$  in seawater are extremely low for a reliable measurement, even for most advanced techniques of trace element measurements. So far, only radiometrically determined values of  $^{227}\text{Ac}$  in seawater have been reported in the literature. The reported activities in seawater range from about 5 dpm/m<sup>3</sup> (83  $\mu\text{Bq/l}$ ) close to the sea-floor in the Southern Ocean to 0.05 dpm/m<sup>3</sup> (0.83  $\mu\text{Bq/l}$ ) at the sea surface far off shore (Geibert et al., 2002). Converting the activities to concentrations, this means that about 830 to 83000 atoms/l have to be detected in a reliable manner. Secondly, its detection via radiation is not straightforward because of the weak energy of the beta and  $\gamma$ -radiation of  $^{227}\text{Ac}$  itself. Therefore, daughter nuclides of  $^{227}\text{Ac}$  have to be detected in order to draw conclusions on  $^{227}\text{Ac}$  activities.

The only isotope of actinium available to be used as a tracer for chemical recovery during the separation and purification steps is  $^{225}\text{Ac}$ , with a half-life of 10 days. This requires either a quick separation of actinium from other nuclides in order to avoid unacceptable losses of the yield tracer by decay, or assumptions on quantitative recovery of actinium when working without a yield tracer. Additionally, the short half-life of  $^{225}\text{Ac}$  also would represent a problem when trying to measure actinium by mass spectrometric techniques.

Here, we propose a radiometric method to measure  $^{227}\text{Ac}$  on about 50 l of sea water, which opens the possibility to get data from oceanographic bottle samples, and we report first results that show the consistency of our method with previous techniques.

## 2. Sampling

The amount of seawater needed for  $^{227}\text{Ac}$  analysis obviously depends on the expected activity, but also on the chemical recovery, the background of the alpha-detectors to be used, and the available time for measurement. In the reported case, the amount was ranging from about 20 L for samples close to the seafloor to 80 L for samples near the surface. The samples are filled into the required number of pre-cleaned 20 L containers made from polycarbonate or polyethylene. Cleaning includes a step with a dilute  $\text{HCl}/\text{H}_2\text{O}_2$  mixture in

order to remove all traces of  $\text{MnO}_2$  present, followed by repeated (at least 3x) rinsing with 18.2 M $\Omega$  water in order to avoid losses due to  $\text{MnO}_2$  dissolution in the following steps. The sample containers should additionally be rinsed with some sample immediately before sampling.

## **2.1. Preparing a $\text{MnO}_2$ precipitate carrying $^{227}\text{Ac}$**

Quantitative recovery of actinium from the sea water samples can be attained by the precipitation of  $\text{MnO}_2$  (comproportionation of manganese in alkaline solution). Briefly, to each 20 L subsample, six drops of an aqueous ammonia solution (25 %), 250  $\mu\text{l}$  of a solution of  $\text{KMnO}_4$  (60 g/l), and 100  $\mu\text{l}$  of a solution of  $\text{MnCl}_2$  (400 g/L  $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ /l) are added, shaken vigorously, and set aside overnight, as described by Rutgers van der Loeff and Moore (1999) for  $^{234}\text{Th}$ . Although we apply here a different approach to determine recoveries of  $\text{MnO}_2$  via  $^{234}\text{Th}$  during sampling (see below), we suggest adding  $^{229}\text{Th}$  spike in equilibrium with  $^{225}\text{Ac}$  before performing the precipitation.

The precipitate containing the actinium can then be recovered by filtration onto 142 mm diameter nucleopore polycarbonate filters. In our case, the filters were folded twice, dried, and then folded to a small square covered by cling film, which was directly beta-counted for  $^{234}\text{Th}$  in order to check for losses of manganese during filtration (for details of the filter geometry see Rutgers van der Loeff and Moore, 1999). This step could be omitted if the sample had already been spiked with  $^{229}\text{Th}$ . A loss of  $\text{MnO}_2$  would also mean a loss of Ac, which therefore has to be quantified, either by directly measuring the recovery for Mn, or by measuring another element that is known to be retained quantitatively by  $\text{MnO}_2$ , like a thorium isotope. We chose  $^{234}\text{Th}$ , for which we knew the actual value either by measurement on independent samples (surface waters), or we could assume an equilibrium value with  $^{238}\text{U}$  for deep water samples. The method for quantitative recovery of the  $\text{MnO}_2$  precipitate has been used for years in the analysis of  $^{234}\text{Th}$ .

The addition of  $^{229}\text{Th}$  directly after sampling would also offer the advantage to contain  $^{225}\text{Ac}$ , which can later be used to control the chemical recovery of the actinium separation. If the recovery is determined by  $^{234}\text{Th}$ , a second beta counting has to be carried out to correct for

background events after complete decay of  $^{234}\text{Th}$ .

The filtrate of six samples (1000 m) was retained after a first  $\text{MnO}_2$ -precipitation step, and a second  $\text{MnO}_2$ -precipitate was formed. This precipitate was used as a verification that the first precipitation was quantitative, and the samples were processed as procedural blanks. The blank contribution was found to be insignificant.

## **2.2. Dissolving the $\text{MnO}_2$ precipitate**

The dry precipitate must be redissolved in presence of the filters. For that purpose, the cling film is removed by means of tweezers, and the folded filter is cut into 3-5 pieces. The cutting procedure is performed in a 50 mL teflon beaker, and all corresponding subsamples (dry filters), each representing one 20 L container from one depth, are put together into one beaker. The  $\text{MnO}_2$  forms a very fine dust that tends to stick to the walls of the beaker. It is advisable to make sure that the teflon beakers are not charged electrostatically, as far as possible. The beakers are placed under a fume hood onto magnetic stirrers. Ten mL hydrochloric acid (2 M) are added, and if not yet present,  $^{229}\text{Th}$  in equilibrium with  $^{225}\text{Ac}$  should be added as well, as a yield tracer. In our case, we used 1-2 dpm of  $^{229}\text{Th}$ , where 2 dpm turned out to be the better choice. It is not advisable to use much higher amounts than 5 dpm, as traces of  $^{229}\text{Th}$  escaping into the Ac fraction might then lead to interferences in the  $^{227}\text{Ac}$  spectra. The samples are dissolved overnight, under permanent stirring. The next day, the acid is decanted into a centrifuge vial, keeping the filter fragments back in the teflon beaker. The residual filter parts are filled up with another 10 mL HCl and kept stirring for another hour. The above procedure is repeated with another 10 mL of HCl. A total of 25 -30 mL of HCl with the sample are now contained in the centrifuge tube. About 100  $\mu\text{L}$  of an iron chloride solution (50 g/L in 0.1 N HCl) are added.

## **2.3. Chemical purification and separation of actinium**

The next purification step of actinium is achieved by co-precipitation with iron as hydroxide, which is quantitative for actinium as well as for thorium and uranium, while radium is less well retained. The precipitate forms when ammonia (25%) is added to the sample until pH 8.5 to 9

is reached. The samples can be filled up with 18.2 MΩ water to 50 mL and centrifuged for 6 minutes @ 4000 rpm. The supernatant can be discarded, and the precipitate of Fe(OH)<sub>3</sub> is re-dissolved with a few drops of 9 N HCl, filled up to 45 mL and precipitated again with ammonia, and centrifuged again. This step is repeated twice. Then, pure water is added, and the precipitate is washed and centrifuged again, the supernatant discarded again. The iron hydroxide is dissolved with concentrated HCl (1:1 by volume) and filled up to 15 mL with 9 N HCl. It is now ready for the first column separation.

The final purification of actinium is done by anion exchange chromatography with three sequential columns. The scheme of column separations is given in form of a table (Table 1). While the first two column types have been introduced to marine radiochemical research by (Anderson and Fleer, 1982), the separation of actinium from radium with Eichrom TRU resin was first described by (Burnett et al., 1995). Please note that the complete conversion of the sample to HNO<sub>3</sub> form is an essential step in the procedure. It is accomplished by carefully evaporating the sample to dryness, adding HNO<sub>3</sub> conc., and evaporating it (repeat two times). In the third step, add some HNO<sub>3</sub> conc. one last time, evaporate it to a small drop, place a drop of water of the same size next to it (in the case of 8 N HNO<sub>3</sub> -if 2 N HNO<sub>3</sub> is desired, add approx. 8 times the volume of the drop), and fill up to the desired volume with the appropriate acid. If some MnO<sub>2</sub> remains in insoluble form at the bottom of the beaker, one may add traces of H<sub>2</sub>O<sub>2</sub> (30%) in order to dissolve it.

**Table 1**

#### **2.4. Electroplating of actinium**

Several methods for electroplating of actinium are available in the literature (Bojanowski et al., 1987; Martin et al., 1995; Alhassanieh et al., 1999). The method that we propose here is not especially designed for actinium, but the very same than previously used for alpha-spectrometric determination of <sup>230</sup>Th or <sup>231</sup>Pa (modified after Anderson and Fleer, 1982). We observed satisfactory electroplating efficiencies for this method, as proven by average total (chemical and counting) yields of the reference samples of 15 ± 5%, which corresponds to chemical recoveries of about 50%. Briefly, the spot in the teflon beaker containing the

actinium is covered with 1 mL of 0.01 N  $\text{HNO}_3$ . A custom made electroplating cell made from teflon, with an anode made of platinum wire and a cathode consisting of a 25 mm diameter silver disc is used for the electroplating. The spot in the beaker with the acid is scratched carefully off the beaker with a pipette tip and filled into the plating cell. The procedure is repeated twice, replacing the dilute nitric acid with a solution of  $\text{NH}_4\text{Cl}$  @ pH 2. Then, it is repeated with one mL of a saturated solution of ammonium oxalate. The electroplating cell containing the mixture is placed on a magnetic stirrer. Electrolysis is performed for exactly one hour with a voltage of 6 V and a starting current of 0.8 A. After a while, the current drops to about 0.1 A, indicating that the electroplating is approaching its end. After one hour, the supernatant is collected in the original teflon beaker (can be discarded when measurement of the yield tracer indicates that the recovery is sufficient). The cell is rinsed twice with pure water, and the silver disc is carefully heated in a blue flame, avoiding partial melting of the silver, but oxidizing the deposited film. The sample is now ready for the first counting.

### **3. Measurement**

#### **3.1. Counting for determination of the total yield**

If Ac is electroplated directly, each sample has to be measured twice. First, it is measured for the yield tracer  $^{225}\text{Ac}$  and its daughters as soon as possible. A second measurement must be performed when the yield tracer has decayed completely, and when the daughters of  $^{227}\text{Ac}$  have approached their maximum activity. The two cases will result in completely different spectra, which are discussed in detail below, because their understanding is the key to the measurement of  $^{227}\text{Ac}$ .

#### **Figure 1**

Counting for  $^{225}\text{Ac}$  should take place as soon as possible after separation of Ac from Th and subsequent electroplating. It is necessary that all Th and Ra have been removed from the sample by the column separation. If this is not the case,  $^{225}\text{Ac}$  is not a reliable yield tracer because it might be produced after the separation of Ac by decay of  $^{225}\text{Ra}$  (half-life 14.8 d). Such contributions may be discovered if peaks from the  $^{229}\text{Th}$  decay chain are found during



the second counting, or if excessive  $^{226}\text{Ra}$  contributions are observed. The activity ratio of  $^{226}\text{Ra}$  to  $^{227}\text{Ac}$  in sea water samples may be very high ( $>1000$ ), so minor  $^{226}\text{Ra}$  peaks may sometimes occur without implying substantial problems in Ra/Ac separation. Although  $^{225}\text{Ra}$  will be lost in the electroplating procedure at the proposed voltages, its presence before electroplating might lead to an overestimation of the chemical yield. A typical spectrum of  $^{225}\text{Ac}$  is shown in Figure 1.

$^{225}\text{Ac}$  itself has a relatively broad peak which is composed of multiple energies. Additionally, its peak is in a region that is also occupied by  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  (a daughter of  $^{227}\text{Ac}$ ), as can be seen on the decay charts of the two involved decay series (Figure 2a and 2b). This peak can therefore not be used for the determination of  $^{225}\text{Ac}$ . The next daughter of  $^{225}\text{Ac}$  is  $^{221}\text{Fr}$ . The main peak of  $^{221}\text{Fr}$  (83% of its decays) is observed at 6.341 MeV, a smaller fraction is found near 6 MeV (various energies), disturbing (and disturbed by) the main peak of  $^{227}\text{Th}$ . The granddaughter of  $^{225}\text{Ac}$ ,  $^{217}\text{At}$ , is best suited for the indirect measurement of  $^{225}\text{Ac}$  or  $^{225}\text{Ra}$  (Martin et al., 1995; Purkl and Eisenhauer, 2004). Virtually all of its decays are observed at a single energy (7.067 MeV), which is not affected by other nuclides. We therefore recommend determining  $^{225}\text{Ac}$  by measurement of  $^{217}\text{At}$ . Losses in the decay chain by recoil effects do not seem to take place, because a comparison of the observed activities of  $^{225}\text{Ac}$ ,  $^{221}\text{Fr}$  and  $^{217}\text{At}$  in undisturbed spectra (no contribution from  $^{226}\text{Ra}$  and daughters) showed good agreement with the values expected for a secular equilibrium.

The obtained value can be expressed as a count rate, and calculated back to the time of separation from  $^{225}\text{Ra}$ , which will be the iron precipitation in case of rapid processing, or the last column if the iron precipitation was stored long enough to allow  $^{225}\text{Ra}$  for ingrowth from  $^{229}\text{Th}$ . The ratio of the count rate to the known disintegrations per minute (dpm) of the spike is an expression of the overall yield of the procedure, including chemical losses and detector efficiencies (Equation 1). If the same detector is used for the second counting, this value can be used to correct for all losses (except  $\text{MnO}_2$  during sampling) in one single step. If the spike is added upon sampling, even the  $\text{MnO}_2$  losses are included in the calculated recovery.

## Figure 2

### 3.2. Growth of the daughters of $^{227}\text{Ac}$

A characteristic of  $^{227}\text{Ac}$  in the radioactive decay of its daughter nuclides is a sequence of two nuclides with relatively similar half-lives ( $^{227}\text{Th}$  with a half-life of 18.72 days, and  $^{223}\text{Ra}$  with a half-life of 11.435 d). Because of this similarity of the half-lives, the establishment of a full equilibrium between  $^{227}\text{Th}$  and  $^{223}\text{Ra}$  (and its short lived daughters) takes about ten half-lives of  $^{227}\text{Th}$  (see Figure 3). As a compromise between equilibrium conditions, complete decay of the  $^{225}\text{Ac}$  yield tracer, and the wish to obtain data as soon as possible, we recommend the measurement of the  $^{227}\text{Ac}$  daughters 100 days after electroplating.

Figure 3

### 3.3. Counting the daughters of $^{227}\text{Ac}$

Figure 4

The sensitivity of the method that we propose here is based on the counting of a number of  $^{227}\text{Ac}$  decay products, which allows detecting multiple events for a single  $^{227}\text{Ac}$  atom present at the time of electroplating. The decay events of  $^{227}\text{Th}$ ,  $^{223}\text{Ra}$ ,  $^{219}\text{Rn}$ ,  $^{215}\text{Po}$ , and  $^{211}\text{Bi}$  can all be included in the calculation of  $^{227}\text{Ac}$  activity. The actual spectra for individual nuclides are relatively complex, with the exception of  $^{215}\text{Po}$ . However, three regions of interest can be found in the spectrum (see Figure 4), each of them representing two nuclides or less. In the region from 5.4-6.1 MeV, we find  $^{223}\text{Ra}$  and  $^{227}\text{Th}$ . In the region from 6.2-6.9 MeV, the decays of  $^{219}\text{Rn}$  and  $^{211}\text{Bi}$  are observed. And the region from 7.3-7.5 MeV is reflecting the decays of  $^{215}\text{Po}$ . The separate acquisition of the three regions is useful for later control of the data for losses due to  $^{219}\text{Rn}$ , or for disturbing contributions from the  $^{232}\text{Th}$  chain, which would be seen in unusually high ratios of group 1 ( $^{227}\text{Th}$ ,  $^{223}\text{Ra}$ ) and 2 ( $^{219}\text{Rn}$ ,  $^{211}\text{Bi}$ ).  $^{215}\text{Po}$  is largely undisturbed by other nuclides and would still give a reliable value if the other energies are influenced by some other isotopes.

### 3.4. Losses in the decay chain due to $^{219}\text{Rn}$ diffusion

Another topic to be discussed is the presence of an intermediate product in gas form,  $^{219}\text{Rn}$ . While one might expect that the short half-life of  $^{219}\text{Rn}$  (3.96 s) is preventing the loss of a

significant proportion of the atoms, this is not quite the case. There is some debate in the literature about the degree of Rn loss on an electroplated source (Jurado Vargas and Fernandez de Soto, 1996; Hancock and Martin, 1996; Vargas, 2001). We chose an empirical approach to quantify the loss for our specific sample type. In our spectra of  $^{227}\text{Ac}$ , we consider three groups of energies, each representing one or two nuclides (for an example see Figure 4). The loss due to  $^{219}\text{Rn}$  was calculated as the sum of events for the groups 2 and 3 ( $^{219}\text{Rn}$ ,  $^{215}\text{Po}$  and  $^{211}\text{Bi}$ ) divided by three, divided by the sum of events for group 1 ( $^{227}\text{Th}$  and  $^{223}\text{Ra}$ ) divided by two. For a total of 21 clean spectra, we obtained a loss of  $2\% \pm 3\%$ , which means that the occurrence of any loss due to  $^{219}\text{Rn}$  is not significant.

### 3.5. Converting the counts to concentrations

Table 2

The first counting period, immediately after electroplating, serves to calculate the counting yield for actinium from  $^{225}\text{Ac}$ . The counting rate as obtained from  $^{217}\text{At}$  during the first counting period is calculated back to the separation from  $^{229}\text{Th}$ , and then compared to the actual  $^{225}\text{Ac}$  activity, as known from the addition of the  $^{229}\text{Th}/^{225}\text{Ac}$  spike:

$$(1) y^{\text{Ac}} = ((n^{217\text{At}} / \Delta t_1) / e^{\lambda^{225\text{Ac}} * (t_2 - t_1)}) / A^{225\text{Ac}}$$

y: overall yield of the separation and measurement procedure, includes chemical losses and detection efficiency- dimensionless, detector specific

n: number of detected disintegration events (counts)

$\lambda$ : decay constant (unit  $1/t$ , t must be in same unit as  $t_1$  and  $t_2$ )

A: known activity of the  $^{225}\text{Ac}$  spike

$t_1, t_2$ : see table 2

Given the yield of the separation and counting steps, the results of the second counting period can be converted into an activity of  $^{227}\text{Ac}$ . In a first step, the counts of the three energy groups, representing the disintegrations of  $^{227}\text{Th}$ ,  $^{223}\text{Ra}$  (group 1),  $^{219}\text{Rn}$ ,  $^{211}\text{Bi}$  (group 2), and  $^{215}\text{Po}$  (group 3) are added and divided by five to give a count rate that represents  $^{223}\text{Ra}$  or one of its daughters.

$$(2) \ n_{t_3}^{223\text{Ra}} / \Delta t_2 = \frac{n_{t_3}^{\text{group1}} + n_{t_3}^{\text{group2}} + n_{t_3}^{\text{group3}}}{5} / \Delta t_2$$

Equation (2) can be modified if the ratio group 1/group 2 indicates contributions from other nuclides in group1, or significant losses of  $^{219}\text{Rn}$  from the source. If the count rate is sufficient, the counts of  $^{215}\text{Po}$  (group 3) can also be taken as representing  $^{223}\text{Ra}$ , not applying equation (2). After a count rate for  $^{223}\text{Ra}$  has been obtained, it can be converted into the number of atoms present in the sample at the time of measurement.

$$(3) \ N_{t_3}^{223\text{Ra}} = \frac{n_{t_3}^{223\text{Ra}} / \Delta t_2}{\lambda^{223\text{Ra}}}$$

N: Number of atoms

$^{223}\text{Ra}$  never reaches a secular equilibrium with  $^{227}\text{Th}$  because their decay constants are too similar (Figure 3). Therefore, the calculation of  $^{227}\text{Ac}$  from the activities of its daughters is not straightforward. Based on the laws of radioactive decay series as taken from (Faure, 1986), the number of  $^{227}\text{Ac}$  atoms can be calculated from the number of  $^{223}\text{Ra}$  atoms:

$$(4) \ N_{t_3}^{227\text{Ac}} = \frac{N_{t_3}^{223\text{Ra}}}{\lambda^{227\text{Ac}} * \lambda^{227\text{Th}} * \left( \frac{e^{\lambda^{227\text{Ac}} * \Delta t_3}}{0.00223242} + \frac{e^{\lambda^{227\text{Th}} * \Delta t_3}}{-0.00086786} + \frac{e^{\lambda^{223\text{Ra}} * \Delta t_3}}{0.00141983} \right)}$$

This number can then be converted into a "virtual" alpha count rate of  $^{227}\text{Ac}$ :

$$(5) \ n_{t_3}^{227\text{Ac}} / \Delta t_2 = N_{t_3}^{227\text{Ac}} * \lambda^{227\text{Ac}}$$

Using the overall yield from equation (1), the count rate can be converted into the actual  $^{227}\text{Ac}$  activity at the time of the second measurement ( $t_3$ )

$$(6) \ A_{t_3}^{227\text{Ac}} = \frac{n_{t_3}^{227\text{Ac}} / \Delta t_2}{y^{\text{Ac}}}$$

If storage between sampling and measurement is significant in regard to the half-life of  $^{227}\text{Ac}$ , a further decay correction becomes necessary:

$$(7) \ A_{t_0}^{227\text{Ac}} = A_{t_3}^{227\text{Ac}} / e^{\lambda^{227\text{Ac}} * (t_3 - t_0)}$$

Obviously, the propagation of the counting error is rather complicated and prone to error, as some requirements are not met (e.g., the detected counts are not stochastically independent events). Such a problem can be addressed either in a mathematical way (Kragten, 1994), or the external reproducibility of the results can be checked on a reference material.

Here, we chose the uranium ore reference material UREM-11 (Hansen and Ring, 1983), which is certified for uranium. It contains uranium in the natural  $^{238}\text{U}/^{235}\text{U}$  atom ratio of 137.88. Its  $^{238}\text{U}$  activity reference value is 44.0 dpm/g, and the derived  $^{235}\text{U}$  ( $=^{231}\text{Pa} = ^{227}\text{Ac}$ ) value is 2.02 dpm/g. The  $^{227}\text{Ac}$  activity of this material was repeatedly measured (three sets of 6 samples each) by the method described above. The only difference was the preparation of the sample by a full digestion instead of  $\text{MnO}_2$  precipitate, and the absence of the last decay correction, because no time elapsed since sampling. The results are presented in Table 3. They suggest an error associated with the method of <10% (1  $\sigma$ ). This is the constant error that we give with the results. Another means of testing the validity of the results is the comparison with other methods, as shown in the following section.

#### 4. Results and comparison with sampling via in situ pumps

Some first results from the Eastern Weddell Gyre are depicted in Figure 5. The data show the typical  $^{227}\text{Ac}$  pattern, an increase with depth. A feature that is unique to the Southern Ocean is the occurrence of comparably high values up to the sea surface, which are due to deep upwelling (Geibert et al., 2002). As everywhere in the ocean, a fraction of  $^{227}\text{Ac}$  is in secular equilibrium with  $^{231}\text{Pa}$  in the water column (supported  $^{227}\text{Ac}$ ) and is not originating from the deep sea floor. Only the  $^{227}\text{Ac}$  activity that is exceeding the value of  $^{231}\text{Pa}$  ( $^{227}\text{Ac}_{\text{ex}}$ ) is of actual significance for the calculation of mixing coefficients or upwelling rates. This  $^{227}\text{Ac}_{\text{ex}}$  is released almost exclusively from deep sea sediments, with only minor contributions from shallow regions (Geibert et al., submitted).

**Figure 5**

A comparison of the method with values obtained by large-volume sampling by in situ pumps

(see Figure 6) reveals an excellent agreement between the methods. A linear regression yields a slope of almost 1:1 with a small constant offset ( $y = 0.96x + 0.20$ ). Table 4 illustrates the sample sizes required for each method, together with some important parameters. The total yield (average 17%, comparable to the reference material) expresses the decay-corrected counts of the  $^{225}\text{Ac}$  spike divided by its initial activity. This yield value integrates the detector efficiency (typically 30%) and the chemical yield. A total yield value of 15% therefore implies a chemical yield of approximately 50%. In addition, we provide information about the total counts (sum of all five measured  $^{227}\text{Ac}$  daughters) for the new method. For the in-situ pump samples, sampling was done according to Geibert et al. (2002), while the chemical separation and measurement was done as described here for obtaining the best possible results. Here, we also provide a value for the sorption efficiency of the  $\text{MnO}_2$ -impregnated cartridges, which is an important term in the calculation of the final  $^{227}\text{Ac}$  activities from in situ pumps. Failures of the pumps and very poor chemical yields in a few cases led to missing values in the final table.

**Table 4**

**Figure 6**

## 5. Concluding remarks

The determination of diapycnal mixing coefficients is of crucial importance for the understanding of oceanic circulation (Egbert and Ray, 2000; Wunsch, 2000), and  $^{227}\text{Ac}$  may serve here as a tracer. The proposed method is a development of  $^{227}\text{Ac}$  measurement techniques for the specific needs of marine science. Comparing it to the measurement of  $^{227}\text{Ac}$  on Mn-fiber by a RaDeCC-system (Moore and Arnold, 1996), we see three main advantages:

- Compared to Shaw and Moore (2002), smaller sample volumes are required
- Compared to Geibert et al. (submitted), the uncertainty of individual measurements is

much lower

- The same sample can be used to measure  $^{231}\text{Pa}$  for  $^{227}\text{Ac}_{\text{ex}}$  calculations.  $\text{MnO}_2$ , our carrier of  $^{227}\text{Ac}$  for sampling, is just as efficient for some other U-Th-series radioisotopes (e.g. Reid et al., 1979).

Especially needful would be the measurement of  $^{231}\text{Pa}$  on the same sample by mass spectrometry, combined with  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{230}\text{Th}$ . This set of tracers is expected to be exceptionally powerful for disentangling the effects of water mass residence times and particle cycling in marine tracer signatures.

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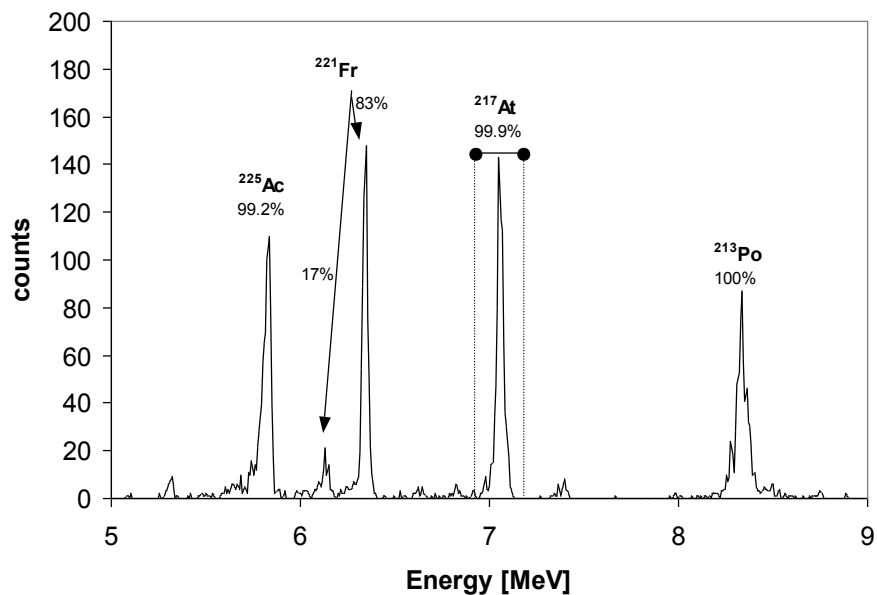


Figure 1:

The spectrum of  $\alpha$ -decays obtained from the first counting. The main peaks are due to the yield tracer  $^{225}\text{Ac}$  and its daughter nuclides, some very small peaks indicate the beginning ingrowth of the daughters of  $^{227}\text{Ac}$  in the electroplated sample.

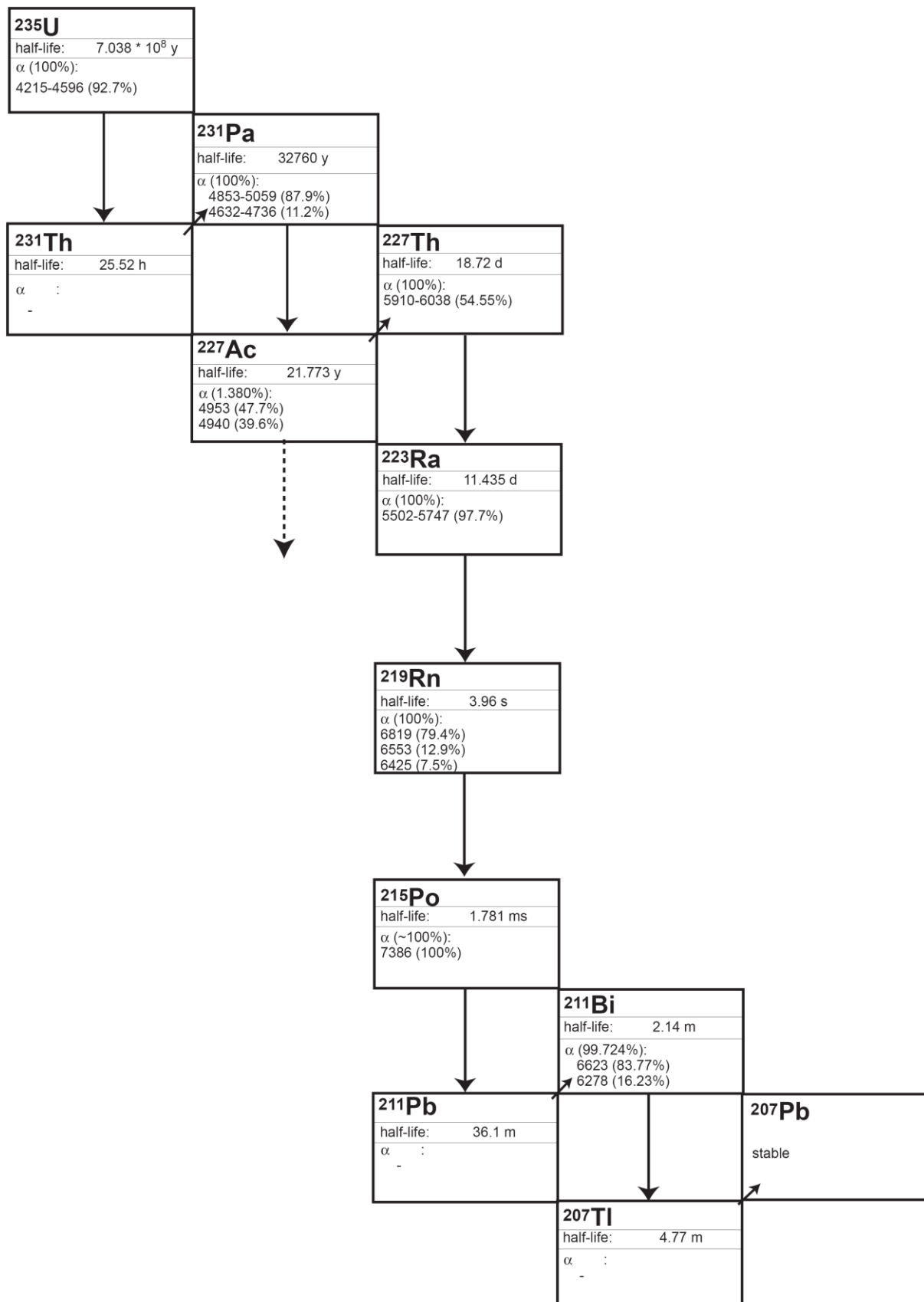


Figure 7 a: The <sup>235</sup>U decay chain with additional information about the energies of the emitted α-particles

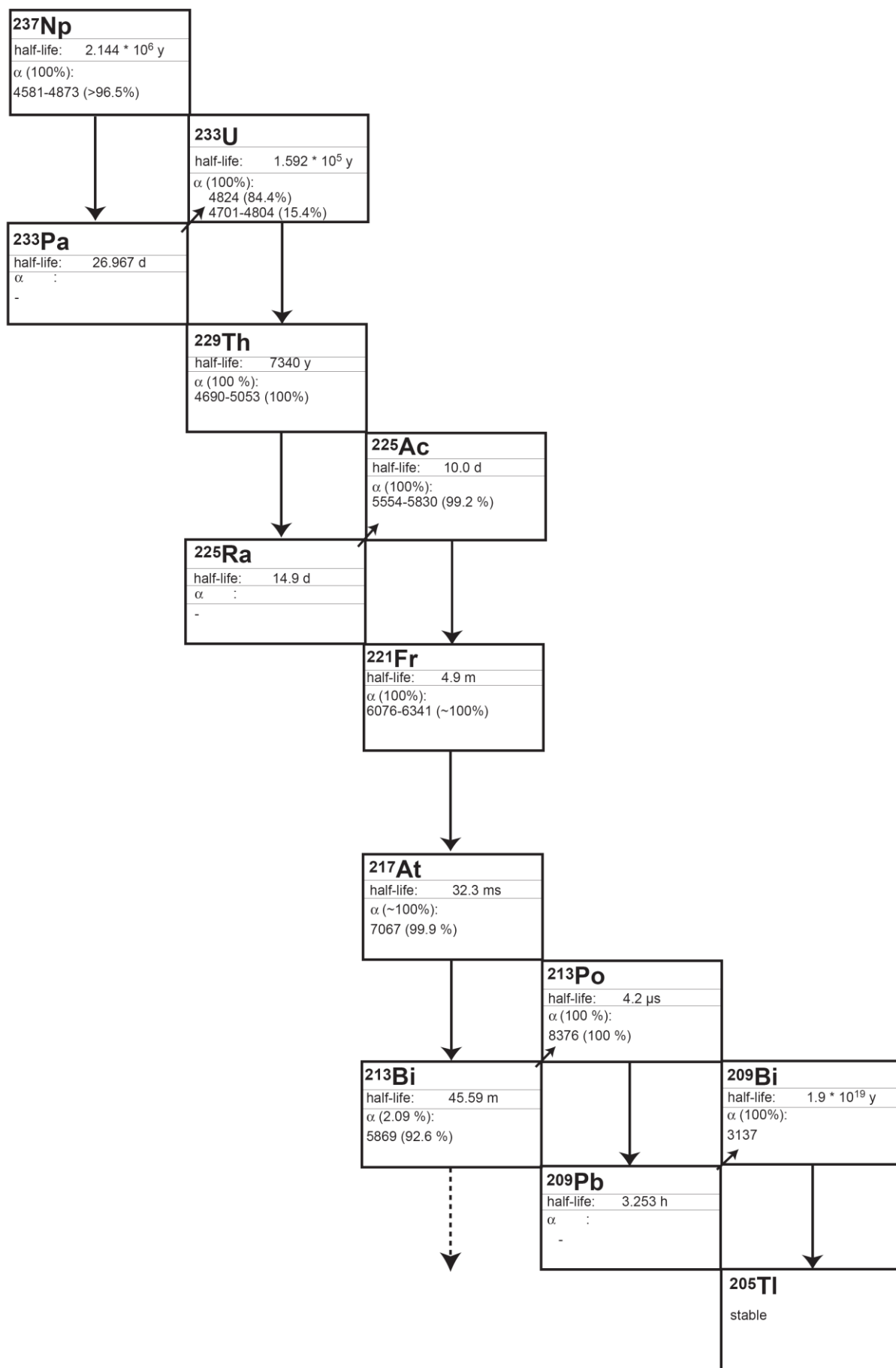


Figure 8 b: The <sup>237</sup>Np decay chain with additional information about the energies of the emitted α-particles

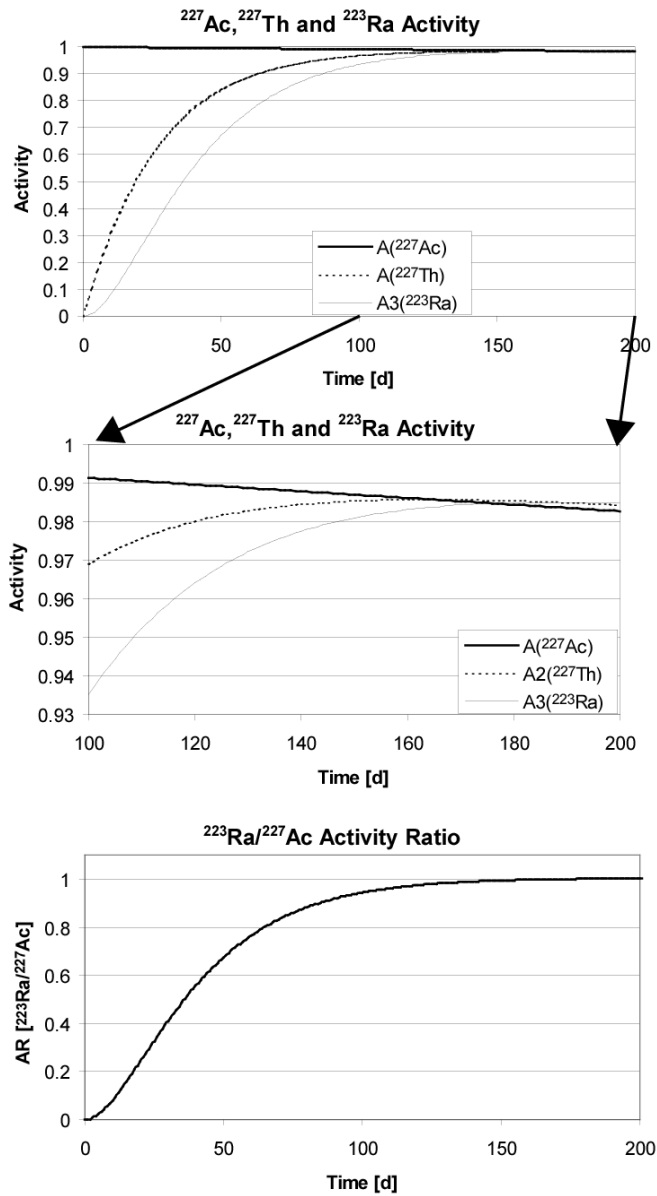


Figure 9:

The growth of  $^{227}\text{Th}$  and  $^{223}\text{Ra}$  activity from a  $^{227}\text{Ac}$  source vs. time. The upper panel depicts the development of the relative activities during 200 days after the initial separation. The middle panel displays the relative activities from 100 to 200 days after separation, which is the foreseen time frame of the second measurement. The activity of all daughters is exceeding 93.5% of the initial  $^{227}\text{Ac}$  activity after 100 days. The lower panel is expressing the activity ratio of  $^{223}\text{Ra}$ ,  $^{219}\text{Rn}$ ,  $^{215}\text{Po}$  and  $^{211}\text{Bi}$  to  $^{227}\text{Ac}$ .

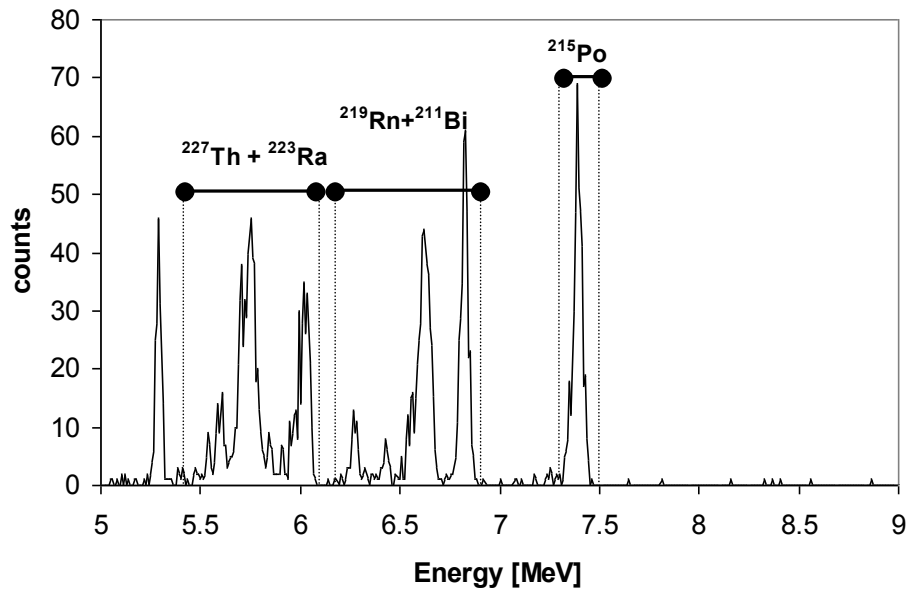


Figure 4:

The spectrum of the same source as in figure 1, after the growth of the  $^{227}\text{Ac}$  decay chain (>100 days). The yield tracer has disappeared. The thick lines indicate the energy intervals of the "groups" mentioned in the text. Left: group 1; middle: group 2; right: group 3.

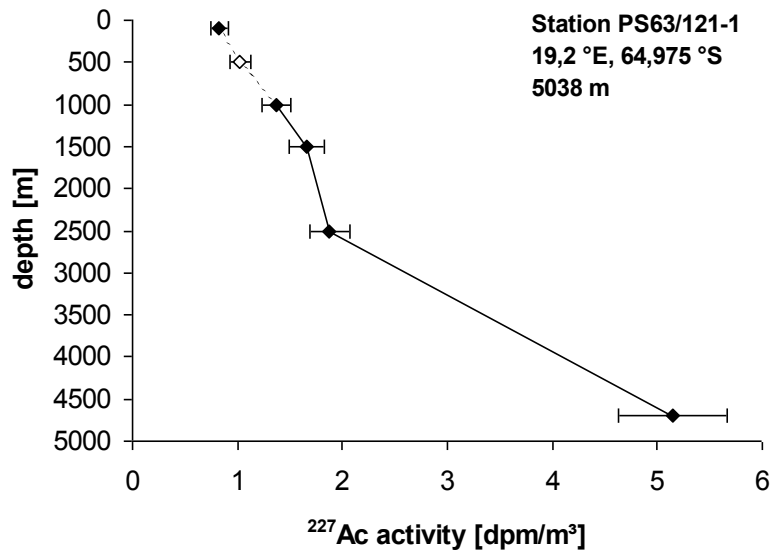


Figure 5:

<sup>227</sup>Ac activities at a station in the Eastern Weddell Gyre as obtained with the new method. The open symbol at 500 m depth indicates a value from the corresponding in situ pump sample, because the CTD sample was lost (poor Ac recoveries). The given error is constantly 10%, which is an estimate based on repeated measurement of a reference material (see text). The actual error is composed of several counting errors (<sup>234</sup>Th for MnO<sub>2</sub> recovery, <sup>225</sup>Ac yield tracer, and <sup>227</sup>Ac daughters, that amount individually to less than 5%). Some minor error sources (weighing of the sample on board, spiking with yield tracer, calibration of counting efficiencies for <sup>234</sup>Th on the MnO<sub>2</sub> source) also contribute to the final error value.

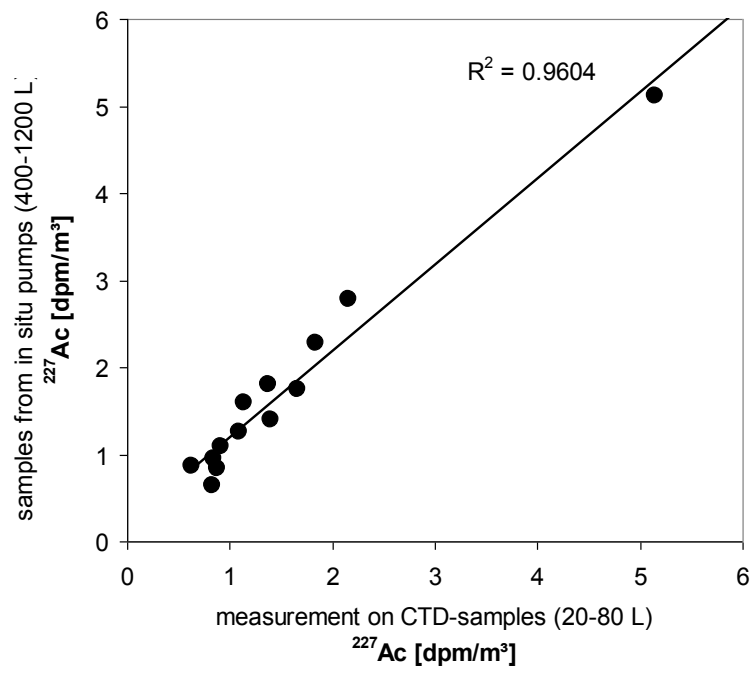


Figure 6:

A comparison of the measurement of  $^{227}\text{Ac}$  in large-volume samples from in situ pumps and in samples taken from the CTD.